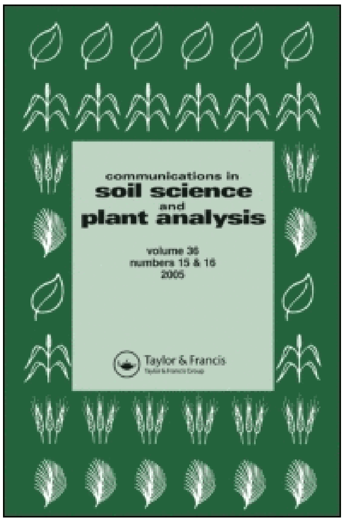


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# Estimation of plant available manganese in acidic subsoil horizons

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# ESTIMATION OF PLANT AVAILABLE MANGANESE IN ACIDIC SUBSOIL HORIZONS

KEY WORDS: Subterranean clover, switchgrass, extractable Mn, soil solution, plant Mn concentration, plant Mn uptake, soil Al.

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## ABSTRACT

General agreement does not exist as to the most appropriate method to estimate plant available Mn in soils. In the current investigation soil and soil solution Mn were measured in limed and unlimed treatments of 11 acidic subsoil horizons and related to plant Mn concentrations, Mn uptake and growth of subterranean clover (*Trifolium subterraneum* L. cv. Mt. Barker) and switchgrass (*Panicum virgatum* cv. Cave-in-Rock). Manganese measurements were taken at planting and harvest and included: Mn extracted by 1$\underline{M}$ $NH_4OAc$ (pH 7), 0.01$\underline{M}$ $CaCl_2$, 0.05$\underline{M}$ $CaCl_2$, 0.033$\underline{M}$ $H_3PO_4$, 0.005$\underline{M}$ DTPA, 0.2% hydroquinone in 1$\underline{M}$ $NH_4OAc$ (pH 7), 0.01$\underline{M}$ $NH_2OH{\cdot}HCl$ in 0.01$\underline{M}$ $HNO_3$, total soil solution Mn and concentrations and activities of $Mn^{2+}$ calculated from the GEOCHEM program. Measured and calculated values of soil solution Mn generally gave the best correlations with subterranean clover and switchgrass Mn concentrations and Mn uptake. Root Mn concentrations were highly correlated with soil solution Mn measurements taken at harvest with r=0.97 and r=0.95 ($p<0.01$) for subterranean clover and switchgrass respectively. The Mn extracted by 0.01M $CaCl_2$ was also significantly correlated ($p<0.01$) with plant Mn concentrations and Mn uptake and proved to be better than the other extractants in estimating plant available Mn. Although Mn concentrations as high as 1769 mg/kg (shoots) and 8489 mg/kg (roots) were found in subterranean clover, Mn did not appear to be the major factor limiting growth. Measures of soil and soil solution Mn were not strongly correlated with yield. Both Al toxicities and Ca deficiencies seemed to be more important than Mn toxicities in limiting growth of subterranean clover and switchgrass in these horizons.



## INTRODUCTION

Manganese toxicity is probably second only to Al toxicity as a growth limiting factor in acid soils (1). A number of properties control Mn availability and cause plant available Mn levels in the soil to vary with time. These properties include: soil pH, total Mn content, soil aeration status, microbial activity, and organic matter content (1).

Several extractants have been used to assess plant available soil Mn, but general agreement does not exist as to the most appropriate method. Soil Mn extracted by 0.01M $CaCl_2$ gave a better correlation with plant Mn concentrations than Mn extracted by $NH_4OAc$ or $NH_4OAc$ plus hydroquinone (2) or soil solution Mn (3). In a study involving wheat and soybean, DTPA extractable Mn gave the best measure of plant available Mn at soil pH values of 5.8 and 6.8 while water was the extractant of choice at pH 4.8 (4). Soil Mn extracted with DTPA gave the highest correlation with Mn concentration in burley tobacco while DTPA, 0.01M $CaCl_2$, 0.033M $H_3PO_4$ and $H_2O$ gave Mn estimates that were significantly correlated with Mn concentrations in rice (5). The Mn extracted by 0.033M $H_3PO_4$ proved to be the best predictor of Mn uptake by sudangrass (6).

Activities of Al species in soil solution (7) and nutrient solution (8) have been related to plant growth limitations. Soil solution Mn, however, has only been measured infrequently (3) in studies that attempt to estimate plant available Mn. The concentration and activity of $Mn^{2+}$ in soil solution may prove to be a useful measure of plant available Mn. The current investigation was therefore undertaken with the following objectives: (i) to compare Mn measured by various extraction methods and soil solution Mn for their ability to predict Mn concentrations and uptake by subterranean clover (_Trifolium_ _subterraneum_ L. cv. Mt. Barker) and switchgrass (_Panicum_ _virgatum_ L. cv. Cave-in-Rock), and (ii) to relate growth limitations exhibited by subterranean clover and switchgrass in unlimed relative to limed treatments of 11 acidic subsoil horizons to soil and soil solution properties.



## MATERIALS AND METHODS

Eleven subsoil horizons from major hill land soils of the Appalachian region were used in the study. The soils were collected by horizon, air dried, and passed through a 2 mm screen. Selected chemical and physical properties of the horizons are shown in Table 1. The horizons were all acidic (pH range 1:1 $H_2O$, 4.39-6.43) with soil Ca and Al saturations ranging from 1.2-66.0% and 1.3-86.2%, respectively (cation saturation = exchangeable cation x 100/CEC).

Nutrients were added in solution form to each soil horizon at the following rates: 90 mg N/kg, 90 mg P/kg, 143 mg K/kg, 13.4 mg S/kg, 0.04 mg Mo/kg, 2.2 mg Cu/kg, 2.2 mg Zn/kg, and 0.4 mg B/kg. Dolomitic lime (calcium carbonate equivalent = 104) was added to half of each horizon sample at a rate of two times the amount of exchangeable Al in the soil. The nutrients and lime were mixed with soil, water was added to bring the moisture content to a level corresponding to 33 kPa tension, and the soils were taken through two wetting and drying cycles over a 2 week

TABLE 1

Series, Subgroup, and Selected Chemical and Physical Properties of the Soils Used in the Investigation.

| Series-horizon | Subgroup | pH 1:1 $H_2O$ | pH 1:1 0:01M$CaCl_2$ | Organic C | Clay | Exchangeable $Ca^a$ | Exchangeable $Mg^a$ | Exchangeable $Al^b$ | $CEC^c$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | ----g/kg---- | | -----------cmol(+)/kg----------- | | | |
| Dandridge E | Lithic Ruptic-Alfic Eutrochrepts | 4.75 | 4.31 | 15.2 | 242 | 2.35 | 0.77 | 2.22 | 6.74 |
| Dandridge Bw | Lithic Ruptic-Alfic Eutrochrepts | 5.20 | 4.70 | 36.4 | 244 | 4.24 | 0.84 | 0.42 | 6.42 |
| Dekalb BE | Typic Dystrochrepts | 4.82 | 4.40 | 13.8 | 82 | 0.18 | 0.10 | 0.89 | 2.08 |
| Dekalb Bw | Typic Dystrochrepts | 4.50 | 4.02 | 3.7 | 102 | 0.12 | 0.07 | 1.59 | 2.38 |
| Dunmore E | Typic Paleudults | 4.81 | 4.30 | 9.2 | 118 | 0.09 | 0.07 | 0.72 | 1.19 |
| Gilpin BA | Typic Hapludults | 4.98 | 4.47 | 25.0 | 248 | 1.50 | 0.93 | 1.40 | 5.13 |
| Lily Bt | Typic Hapludults | 4.45 | 4.00 | 6.8 | 184 | 0.08 | 0.03 | 2.78 | 3.58 |
| Porters Bw | Umbric Dystrochrepts | 4.41 | 4.00 | 5.0 | 132 | 0.05 | 0.02 | 3.56 | 4.13 |
| Tate BA | Typic Hapludults | 4.39 | 4.11 | 82.1 | 139 | 0.70 | 0.40 | 3.47 | 5.91 |
| Watauga Bt | Typic Hapludults | 6.43 | 5.92 | 8.7 | 204 | 2.13 | 1.23 | 0.05 | 3.81 |
| Westmoreland E | Typic Hapludalfs | 4.99 | 4.50 | 27.8 | 113 | 0.90 | 0.36 | 0.87 | 3.62 |

[a] 1M $NH_4OAc$ (pH 7)
[b] 1M KCl
[c] The cation exchange capacity (CEC) was calculated by summation of exchangeable bases and exchangeable acidity.

period. Three replications of the limed and unlimed treatments of each soil were placed in 1450 $cm^3$ plastic pots and seeded to subterranean clover or switchgrass. After emergence, subterranean clover and switchgrass were thinned to 9 and 11 plants per pot, respectively.

The subterranean clover and switchgrass were grown in a greenhouse under natural light with an average day temperature of 25°C and a night temperature of 20°C. Pots were watered daily to bring the soil moisture to a level corresponding to 33 kPa tension. Subterranean clover and switchgrass were harvested after 5 weeks of growth. Shoots and roots were washed free of soil and oven dried at 65°C for 4 days. Dry weights were measured, plant materials were ground, digested in concentrated $HNO_3$-$HClO_4$, and analyzed for Mn and Fe using ICP emission spectroscopy.



Manganese determinations were made at planting and at harvest. Soil samples were taken from the pots at the moisture conditions maintained during the experiment. Ten grams of moist soil were shaken with a given volume of extractant for a specified time. The suspensions were filtered and Mn in the filtrate was determined by ICP emission spectroscopy. Moisture contents were determined and Mn concentrations calculated relative to the dry weight of soil. Extractants, extractant volume, and shaking times were as follows: (i) 1$\underline{M}$ $NH_4OAc$ (pH 7), 50 ml, 30 min (6); (ii) 0.005$\underline{M}$ DTPA (containing 0.01$\underline{M}$ $CaCl_2$ and 0.1$\underline{M}$ triethanolamine pH 7.3), 20 ml, 2 h (9); (iii) 0.01$\underline{M}$ $CaCl_2$, 20 ml, 16 h (2); (iv) 0.05$\underline{M}$ $CaCl_2$, 100 ml, 1 h (10); (v) 0.033$\underline{M}$ $H_3PO_4$, 50 ml, 1 h (6); and (vi) 1$\underline{M}$ $NH_4OAc$ pH 7 containing 0.2% hydroquinone (to quantify easily reducible Mn), 100 ml, 30 min then intermittently for 6 h (11). Manganese oxides were determined by shaking 0.5 g of air dried soil (which had been ground to pass a 60 mesh sieve) with 25 ml of 0.1$\underline{M}$ $NH_2OH \cdot HCl$ in 0.01$\underline{M}$ $HNO_3$ for 30 min (11).

Soil solutions were removed by centrifugation (12) at planting and at harvest. Soil solution pH and electrical conductivity were measured immediately. Total concentrations of K, Ca, Mg, Na, Al, Mn, P and Fe in soil solution were determined with ICP emission spectroscopy. Ion chromatography was used to measure $SO_4^{2-}$, $NO_3^-$, $F^-$, and $Cl^-$ concentrations in soil solution. Dissolved organic C in soil solution was estimated spectrophotometrically (13). The amount of Al reacting with 8-hydroxyquinoline (14) in 15 sec was used as an estimate of reactive Al in soil solution. A modified version (15) of the GEOCHEM computer program (16) containing equilibrium constants from Lindsay (17) was used to calculate concentrations and activities of free ions and complexes in soil solution.

Post harvest soil samples were analyzed for: soil pH 1:1 $H_2O$ and 1:1 0.01M $CaCl_2$; exchangeable bases (18); exchangeable acidity and Al (19); and organic C using a Leco CHN 600. Statistical Analysis System (SAS) programs were used to calculate regression equations and correlation coefficients relating measures of soil and soil solution Mn and other soil properties to growth, plant Mn concentrations and Mn uptake by subterranean clover and switchgrass.



## RESULTS AND DISCUSSION

In the current study Mn extractions and soil solution removal were performed on moist soils. Goldberg and Smith (10) found that soil-extractable Mn levels were increased with air drying. They suggested that it may be preferable to analyze soil in a field-moist state. Soil and soil solution Mn values determined at planting and at harvest are listed in Table 2.

The soil horizons used in this study contained a wide range of Mn oxide concentrations as indicated by the $MnO_2$ values given in Table 2. For a given horizon $MnO_2$ and easily reducible Mn did not change with time or treatment. Mean values across all horizons for unlimed and limed treatments were 745 and 734 mg/kg and 368 and 374 mg/kg for $MnO_2$ and easily reducible Mn, respectively.

TABLE 2

Soil and Soil Solution Mn Concentrations at Planting and Harvest in Unlimed and Limed Treatments of 11 Acidic Subsoil Horizons.

| Horizon | Soil Extractable Mn | | | | | | | Soil Solution Mn | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $MnO_2$ | Easily reducible | 1$\underline{M}$ $NH_4OAc$ | 0.01$\underline{M}$ $CaCl_2$ | 0.05$\underline{M}$ $CaCl_2$ | 0.005$\underline{M}$ DTPA | 0.033$\underline{M}$ $H_3PO_4$ | Total Mn Conc. | $Mn^{2+}$ Conc. | $Mn^{2+}$ Activity |
| | mg/kg | | | | | | | µ$\underline{M}$ | | |
| Dandridge E | 1118[a] | 581[a] | 41.9,19.1[b] | 28.8,16.8 | 50.4,27.1 | 59.7,58.6 | 68.3,50.2 | 140,167 | 134,160 | 101,115 |
| Dandridge E(L)[c] | 1146 | 634 | 2.0,1.6 | 0.8,1.8 | 4.9,4.1 | 24.8,23.6 | 34.8,33.2 | 18.2,14.8 | 16.1,13.9 | 11.0,9.2 |
| Dandridge Bw | 941 | 518 | 0.1,1.6 | 1.1, 3.8 | 2.9,7.2 | 20.0,26.0 | 25.0,35.4 | 2.4,7.6 | 2.1,7.2 | 1.5,5.6 |
| Dandridge Bw (L) | 902 | 493 | 0.1,2.3 | 1.0,3.8 | 2.4,6.9 | 15.7,24.1 | 25.2,31.8 | 2.2,8.1 | 2.0,7.6 | 1.5,6.1 |
| Dekalb BE | 779 | 428 | 16.6,19.3 | 18.4,29.1 | 15.7,36.9 | 29.3,50.5 | 53.6,71.8 | 409,378 | 346,345 | 249,247 |
| Dekalb BE (L) | 769 | 379 | 5.9,4.4 | 3.0,2.6 | 6.4,3.6 | 14.4,8.7 | 64.1,50.7 | 3.6,8.4 | 2.7,7.5 | 1.6,3.9 |
| Dekalb Bw | 207 | 99 | 31.7,27.5 | 33.6,34.0 | 36.6,33.9 | 31.9,39.5 | 45.9,46.5 | 457,1245 | 414,1201 | 313,784 |
| Dekalb Bw (L) | 199 | 115 | 0.4,1.9 | 0.3,0.8 | 0.3,1.5 | 2.7,4.9 | 18.4,31.4 | 1.3,15.1 | 1.0,12.4 | 0.6,7.6 |
| Dunmore E | 56 | 22 | 1.7,4.5 | 3.1,5.6 | 2.6,6.6 | 2.7,7.5 | 8.6,11.8 | 22.2,94.1 | 19.4,87.5 | 14.6,65.9 |
| Dunmore E (L) | 57 | 21 | 2.2,1.5 | 1.6,0.5 | 2.1,0.6 | 2.5,1.9 | 10.6,12.3 | 11.6,12.2 | 9.4,11.4 | 5.7,6.7 |
| Gilpin BA | 2885 | 1346 | 3.8,3.2 | 11.9,9.5 | 13.2,18.0 | 62.4,65.6 | 65.4,59.3 | 21.1,33.4 | 20.0,32.8 | 16.3,24.5 |
| Gilpin BA (L) | 2858 | 1433 | 0.2,1.1 | 0.2,2.0 | 2.3,6.0 | 42.0,37.6 | 42.6,42.4 | 2.7,2.9 | 2.5,2.8 | 1.9,2.1 |
| Lily Bt | 43 | 7 | 12.0,8.9 | 10.0,9.0 | 11.8,11.2 | 9.1,10.9 | 7.8,10.2 | 49.7,411 | 47.6,405 | 39.8,272 |
| Lily Bt (L) | 47 | 17 | 0.1,0.4 | 0.1,0.1 | 0.2,0.1 | 0.8,0.9 | 7.2,9.9 | 0.4,1.7 | 0.3,1.4 | 2.0,0.7 |
| Porters Bw | 100 | 36 | 5.5,5.3 | 7.0,7.3 | 6.9,6.8 | 4.8,6.5 | 4.9,7.7 | 20.9,180 | 20.3,179 | 17.6,130 |
| Porters Bw (L) | 124 | 42 | 0.9,0.5 | 0.4,0.4, | 0.9,0.9 | 1.2,1.3 | 6.8,9.3 | 9.1,2.6 | 7.2,2.3 | 4.3,1.3 |
| Tate BA | 391 | 178 | 67.0,61.6 | 57.4,62.2 | 104.4,94.0 | 74.0,90.0 | 85.8,102.0 | 470,191 | 465,188 | 332,148 |
| Tate BA (L) | 348 | 170 | 58.9,10.0 | 25.6,9.2 | 77.4,18.0 | 68.9,19.2 | 64.6,31.3 | 141,31.8 | 136,31.0 | 91.5,17.3 |
| Watauga Bt | 42 | 18 | 0.05,0.1 | 0.03,0.1 | 0.06,0.4 | 1.0,1.2 | 6.1,7.4 | 0.4,0.8 | 0.4,0.1 | 0.3,0.1 |
| Watauga Bt (L) | 46 | 15 | 2.05,0.1 | 0.01,0.2 | 0.06,0.3 | 0.6,1.0 | 5.2,6.4 | 0.4,0.4 | 0.4,0.4 | 0.3,0.3 |
| Westmoreland E | 1636 | 811 | 22.2,4.4 | 28.4,11.3 | 33.8,17.3 | 97.2,87.0 | 77.8,62.2 | 195,31.5 | 177,29.9 | 136,23.7 |
| Westmoreland E(L) | 1582 | 791 | 1.9,0.8 | 0.1,0.1 | 2.9,2.1 | 53.6,37.4 | 46.4,36.5 | 107,0.7 | 91.1,0.6 | 61.5,0.4 |

[a]Mean value for samples analyzed at planting and harvest.

[b]Mean values are listed for duplicate samples analyzed at planting and at harvest, respectively.

[c]L = Limed treatments.

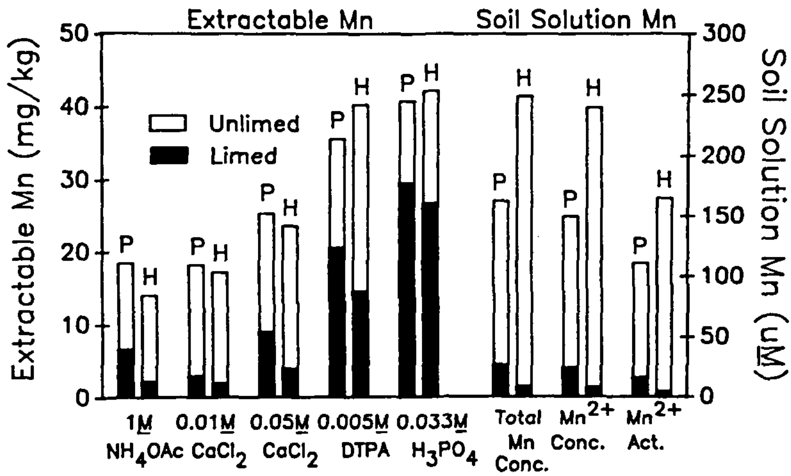


FIGURE 1. Mean Values of Extractable Mn (mg/kg) and Soil Solution Mn (μM) at Planting (P) and Harvest (H) in Unlimed and Limed Treatments of 11 Soil Horizons.

The amount of Mn extracted varied with the soil and the extractant. Mean soil Mn values at planting and harvest are shown for unlimed and limed treatments in Fig. 1. Extraction with 0.033M $H_3PO_4$ and 0.005M DTPA gave the highest Mn values, while extraction with 0.01M $CaCl_2$ and 1M $NH_4OAc$ (pH 7) gave the lowest Mn values. In general extractable Mn values were similar in the samples taken at planting and at harvest for unlimed treatments. Extractable Mn values were, however, lower at harvest than at planting for the limed samples. These findings may reflect continued reaction of the liming material with the soils during the course of the experiment. Liming consistently reduced extractable Mn levels for all extractants and all horizons utilized. The amount of Mn extracted by 0.033M $H_3PO_4$ was least sensitive to liming when compared to the other extractants. The amount of Mn extracted by 0.033M $H_3PO_4$ from the limed horizons represented 72.5% at planting and 63.5% at harvest of the Mn found in unlimed horizons. By way of contrast, the values were 16% and 12% at planting and harvest, respectively, when 0.01M $CaCl_2$ was used as the extractant. It seems likely that extraction of limed samples with 0.033M $H_3PO_4$ would result in an overestimation of plant available Mn.

Measured values for total soil solution Mn and concentrations and activities of $Mn^{2+}$ calculated using the GEOCHEM program are shown in Table 2. Soil solution Mn values displayed much greater changes between planting and harvest than the extractable Mn measurements (Fig. 1). Large differences were noted between soil solution Mn values at planting and harvest for the Dekalb Bw, Dunmore E, Lily Bt, Porters Bw, Tate BA, and Westmoreland E horizons. In the majority of these cases the Mn levels in soil solution increased with time. These results may reflect the greater sensitivity of soil solution Mn measurements to changes in plant available Mn with time.

Shoot and root dry weights, Mn concentrations and Mn uptake are shown for subterranean clover and switchgrass in Table 3. Dry matter production of both subterranean clover and switchgrass varied with horizon and treatment. Switchgrass was less sensitive than subterranean clover to the acidic conditions found in unlimed soil horizons. Switchgrass shoot and root growth increased significantly with liming in 7 of the 11 horizons tested while subterranean clover responded to lime additions in 9 of 11 horizons.

Manganese concentration ranges in the shoots of subterranean clover and switchgrass were 33 - 1769 mg/kg and 34 - 941 mg/kg, respectively. Root Mn concentrations in subterranean clover exhibited a low of 38 mg/kg in the Watauga Bt limed treatment and a high of 8489 mg/kg in the unlimed Dekalb Bw horizon. Manganese concentrations in switchgrass roots ranged from 21 mg/kg in the limed Lily Bt horizon to 1823 mg/kg in unlimed Dekalb Bw. Shoot and root Mn concentrations were generally lower in switchgrass than subterranean clover and probably are the result of a dilution effect associated with the much greater growth displayed by switchgrass across all horizons and treatments. As a result of

TABLE 3
Shoot and Root Dry Weight, Mn Concentrations, and Mn Uptake of Subterranean Clover and Switchgrass Grown in Unlimed and Limed Treatments of 11 Subsoil Horizons.

| | Subterranean Clover | | | | | | Switchgrass | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Shoot | | | Root | | | Shoot | | | Root | | |
| Horizon | Dry weight | Mn conc. | Mn[a] uptake | Dry weight | Mn conc. | Mn uptake | Dry weight | Mn conc. | Mn uptake | Dry weight | Mn conc. | Mn uptake |
| | --g-- | mg/kg | mg/9 plants | -g- | mg/kg | mg/9 plants | -g- | mg/kg | mg/11 plants | -g- | mg/kg | mg/11 plants |
| Dandridge E | 5.89[b] | 604 | 3.56 | 1.67 | 169 | 0.28 | 9.67 | 263 | 2.54 | 2.43 | 263 | 0.64 |
| Dandridge E (L)[c] | 7.18 | 149 | 1.07 | 1.93 | 121 | 0.23 | 11.45 | 139 | 1.59 | 2.78 | 140 | 0.39 |
| Dandridge Bw | 6.76 | 207 | 1.40 | 1.96 | 110 | 0.22 | 11.88 | 158 | 1.88 | 3.38 | 168 | 0.57 |
| Dandridge Bw (L) | 7.17 | 279 | 2.00 | 1.94 | 232 | 0.45 | 12.17 | 143 | 1.74 | 3.55 | 155 | 0.55 |
| Dekalb BE | 1.78 | 1349 | 2.40 | 0.70 | 1027 | 0.72 | 8.01 | 482 | 3.86 | 1.78 | 634 | 1.13 |
| Dekalb BE (L) | 3.72 | 152 | 0.56 | 1.30 | 193 | 0.25 | 11.20 | 126 | 1.41 | 3.29 | 165 | 0.54 |
| Dekalb Bw | 0.78 | 1714 | 1.34 | 0.28 | 8489 | 2.38 | 5.26 | 941 | 4.95 | 1.13 | 1823 | 2.06 |
| Dekalb Bw (L) | 3.89 | 147 | 0.57 | 1.64 | 249 | 0.41 | 9.50 | 103 | 0.98 | 2.93 | 115 | 0.34 |
| Dunmore E | 1.50 | 310 | 0.46 | 0.45 | 364 | 0.16 | 5.88 | 185 | 1.09 | 1.05 | 108 | 0.11 |
| Dunmore E (L) | 5.33 | 114 | 0.61 | 1.89 | 106 | 0.20 | 13.28 | 55 | 0.73 | 4.69 | 54 | 0.25 |
| Gilpin BA | 2.89 | 421 | 1.22 | 1.06 | 485 | 0.51 | 9.81 | 260 | 2.55 | 3.62 | 273 | 0.99 |
| Gilpin BA (L) | 4.46 | 149 | 0.66 | 1.44 | 229 | 0.33 | 10.50 | 157 | 1.65 | 3.32 | 118 | 0.39 |
| Lily Bt | 0.21 | 1056 | 0.22 | 0.05 | 1154 | 0.06 | 0.57 | 733 | 0.42 | 0.09 | 557 | 0.05 |
| Lily Bt (L) | 1.96 | 49 | 0.10 | 0.84 | 65 | 0.06 | 7.51 | 34 | 0.26 | 2.31 | 21 | 0.05 |
| Porters Bw | 0.08 | 1663 | 0.13 | 0.02 | 1000 | 0.02 | 0.10 | 866 | 0.09 | 0.02 | 538 | 0.01 |
| Porters Bw (L) | 1.57 | 108 | 0.17 | 0.74 | 88 | 0.06 | 5.50 | 119 | 0.66 | 1.82 | 51 | 0.09 |
| Tate BA | 1.05 | 1769 | 1.86 | 0.39 | 1621 | 0.63 | 3.91 | 780 | 3.05 | 1.24 | 554 | 0.69 |
| Tate BA (L) | 3.00 | 256 | 0.77 | 0.73 | 243 | 0.18 | 7.13 | 244 | 1.74 | 2.27 | 157 | 0.36 |
| Watauga Bt | 2.15 | 33 | 0.07 | 0.67 | 40 | 0.03 | 3.93 | 71 | 0.28 | 1.10 | 30 | 0.03 |
| Watauga Bt (L) | 1.61 | 34 | 0.06 | 0.49 | 38 | 0.02 | 3.38 | 73 | 0.25 | 0.93 | 26 | 0.02 |
| Westmoreland E | 3.89 | 697 | 2.71 | 1.21 | 1159 | 1.40 | 14.72 | 300 | 4.42 | 4.28 | 363 | 1.55 |
| Westmoreland E(L) | 5.01 | 98 | 0.49 | 1.33 | 263 | 0.35 | 15.06 | 92 | 1.39 | 4.33 | 102 | 0.44 |

[a]Mn uptake = [Dry weight (kg)] [Mn conc. (mg/kg)]
[b]Values in the table represent a mean from three replications.
[c]L = Limed treatments.

greater growth, the amount of Mn taken up by switchgrass was generally higher (Table 3).

Plant Mn concentrations associated with toxicity vary with plant species, genotype within species, and environmental conditions (1). Manganese toxicity symptoms have been reported (20) to appear in subterranean clover when leaf Mn concentrations exceeded 710 mg/kg. However, in another investigation (3) subterranean clover was found to display Mn toxicity symptoms only when plant Mn concentrations exceeded 2600 mg/kg and the soils contained >50 mg/kg of Mn extracted with 0.01$\underline{M}$ $CaCl_2$. In the current investigation shoot Mn concentrations exceeded 710 mg/kg in several of the unlimed horizons (Table 3) but did not go as high as 2600 mg/kg. These results illustrate the difficulty of using plant Mn concentrations as a means of assessing Mn toxicities. Some investigators (21,22) have concluded that plant Mn concentrations are not a good indicator of Mn toxicity.

Temple-Smith and Koen (23) indicated that sensitivity to Mn toxicity may be related to the tendency of some plants to translocate a high proportion of absorbed Mn to plant tops. In the current study, switchgrass seemed to be more tolerant of acid soil conditions than subterranean clover even though it had a higher percentage of total plant Mn in the shoots (80.5%) than subterranean clover (72.7%).

Several investigators (24,25) have used the Fe/Mn ratio in shoots as an indicator of Mn toxicity. Values of <1.5 for the Fe/Mn ratio have been associated with Mn toxicity for a number of crops. In the current investigation, shoot Fe/Mn ratios in unlimed treatments ranged from 0.19 to 17.76 and 0.20 to 3.24 for subterranean clover and switchgrass, respectively (data not shown). The shoot Fe/Mn ratio was <1.5 in all but two unlimed horizons for switchgrass and one unlimed horizon for subterranean clover. Liming increased the Fe/Mn ratio in the shoots of both subterranean clover and switchgrass. Average values of Fe/Mn across all limed horizons were 3.6 for subterranean clover and

2.4 for switchgrass. It is unclear, however, if the low shoot Fe/Mn ratios found in the unlimed treatments in this study are indicative of Mn toxicities.

Correlation coefficients relating subterranean clover and switchgrass shoot and root dry weight, Mn concentrations, and Mn uptake to measures of soil and soil solution Mn at planting and harvest are shown in Table 4. Mean values of soil and soil solution Mn, plant growth, and Mn parameters from limed and unlimed treatments of each of the 11 horizons were used in the correlations. The values for $MnO_2$ and easily reducible Mn did not change with liming and are not included in the correlations. In general the correlations found using Mn values obtained at harvest and at planting were similar although the correlations may be somewhat better when using the Mn parameters obtained at harvest.

Subterranean clover and switchgrass root and shoot dry weight was not significantly correlated with Mn obtained using any of the five extractants. A significant negative correlation ($p<0.05$) was found between soil solution Mn and switchgrass shoot dry weight and subterranean clover and switchgrass root dry weight. These significant correlations only occurred when soil solution Mn values taken at harvest were used in the correlation. These findings suggest that Mn is not the primary factor limiting growth of subterranean clover and switchgrass in the unlimed horizons used in this study.

Total soil solution Mn concentration and concentrations and activities of $Mn^{2+}$ calculated using the GEOCHEM program (16) were the Mn parameters most closely related to plant Mn concentrations and Mn uptake. Root Mn concentrations were highly correlated ($p<0.01$) with soil solution Mn measurements taken at harvest ($r= 0.97$ and $r=0.95$ for subterranean clover and switchgrass, respectively). In this experiment total soil solution Mn concentration, $Mn^{2+}$ concentration and $Mn^{2+}$ activity were highly correlated ($r=0.99$; $p<0.01$). Any of the three soil solution Mn parameters could have been used to predict Mn concentra-

TABLE 4
Correlation Coefficients Relating Subterranean Clover and Switchgrass Shoot and Root Dry Weight, Mn Concentrations and Mn Uptake[a] to Measures of Soil and Soil Solution Mn at Planting and Harvest.

| | Soil Extractable Mn | | | | | Soil Solution Mn | | |
|---|---|---|---|---|---|---|---|---|
| Plant Parameter (N=22) | 1M $NH_4OAc$ | 0.01M $CaCl_2$ | 0.05M $CaCl_2$ | 0.005M DTPA | 0.033M $H_3PO_4$ | Total Mn | $Mn^{2+}$ Concentration | $Mn^{2+}$ Activity |
| Subterranean Clover (soil values taken at planting) | | | | | | | | |
| Shoot dry weight | NS | NS | NS | NS | NS | NS | NS | NS |
| Shoot Mn concentration | .55** | .72** | .53* | NS | NS | .77** | .78** | .79** |
| Shoot Mn Uptake | .50* | .60** | .48* | .65** | .69** | .52* | .52* | .53* |
| Root dry weight | NS | NS | NS | NS | NS | NS | NS | NS |
| Root Mn concentration | NS | .49* | NS | NS | NS | .67** | .66** | .68** |
| Root Mn uptake | NS | .56** | NS | .44* | .47* | .71** | .70** | .72** |
| Subterranean Clover (soil values taken at harvest) | | | | | | | | |
| Shoot dry weight | NS | NS | NS | NS | NS | NS | NS | NS |
| Shoot Mn concentration | .66** | .71** | .62** | NS | NS | .76** | .76** | .78** |
| Shoot Mn uptake | .54** | .65** | .61** | .80** | .79** | .56** | .55** | .56** |
| Root dry weight | NS | NS | NS | NS | NS | -.42* | -.42* | -.44* |
| Root Mn concentration | .55** | .64** | .49* | NS | NS | .97** | .97** | .97** |
| Root Mn uptake | NS | .54** | .46* | .69** | .67** | .63** | .63** | .63** |
| Switchgrass (soil values taken at planting) | | | | | | | | |
| Shoot dry weight | NS | NS | NS | NS | NS | NS | NS | NS |
| Shoot Mn concentration | .51* | .65** | .48* | NS | NS | .67** | .67** | .69** |
| Shoot Mn uptake | .52* | .70** | .51* | .69** | .75** | .79** | .78** | .79** |
| Root dry weight | NS | NS | NS | NS | NS | NS | NS | NS |
| Root Mn concentration | NS | .58** | NS | NS | NS | .74** | .73** | .76** |
| Root Mn uptake | NS | .58** | NS | .59** | .65** | .71** | .69** | .70** |
| Switchgrass (soil values taken at harvest) | | | | | | | | |
| Shoot dry weight | NS | NS | NS | NS | NS | -.42* | -.43* | -.44* |
| Shoot Mn concentration | .75** | .81** | .73** | .47* | .47* | .71** | .71** | .74** |
| Shoot Mn uptake | .44* | .50* | .52* | .77** | .70** | .56** | .55** | .56** |
| Root dry weight | NS | NS | NS | NS | NS | -.46* | -.46* | -.47* |
| Root Mn Concentration | .46* | .53* | NS | NS | NS | .95** | .95** | .94** |
| Root Mn uptake | NS | .53* | NS | .54** | .51* | .76** | .76** | .75** |

[a]Mn uptake = [Dry weight/kg)] [Mn conc. (mg/kg)]
*,**Significant at the 0.05 and 0.01 levels, respectively.
NS = Not significant.

tions and Mn uptake by subterranean clover and switchgrass. Total soil solution Mn concentration would be the easiest of the three to obtain. Additional measurements and calculations are needed to obtain $Mn^{2+}$ activities. However, the calculation of activities allows for comparison of plant available Mn across soil solutions of widely different ionic strength.

Based upon correlation coefficients (Table 4), Mn extracted with 0.01<u>M</u> $CaCl_2$ gave the best overall correlation with plant Mn concentration and Mn uptake when compared to the other four extraction techniques. Other investigators (2,3) have noted the suitability of 0.01<u>M</u> $CaCl_2$ as an extractant to estimate plant available Mn. In one study (3) 0.01<u>M</u> $CaCl_2$ extractable Mn was a better predictor of the Mn concentration in subterranean clover than soil solution Mn concentration. Results of the current study suggest that extraction of soils with 0.01<u>M</u> $CaCl_2$ gives a reasonably estimate of plant available Mn and the values are easier to obtain than soil solution Mn.

Multiple regression equations relating subterranean clover and switchgrass shoot and root growth, Mn concentrations and Mn uptake to soil and soil solution properties are shown in Table 5. Soil and soil solution properties measured at harvest were used in the regression equations. The equations listed in Table 5 are all significant ($p<0.01$) and contain from 2 to 5 independent variables based on a criterion of significant ($p<0.05$) increase in $R^2$ with each added term.

Regression equations for subterranean clover and switchgrass shoot and root growth contain expressions for Al and Ca as well as Mn. These results along with the poor correlations (Table 4) found between Mn and growth suggest that factors other than Mn may be responsible for the growth limitations observed in unlimed soil horizons. Dissolved organic carbon (DOC) in soil solution appears in all of the regression equations for root and shoot growth (Table 5). Organically complexed forms of Al have been shown to be nonphytotoxic (26). High levels of DOC in soil solution may serve to partially ameliorate Al phytotoxicity.

TABLE 5

Multiple Regression Equations Relating Subterranean Clover and Switchgrass Shoot and Root Growth, Mn Concentrations, and Mn Uptake[a] to Soil and Soil Solution Properties.[b]

| Dependent Variable | Equation | $R^2$ (N=22) |
|---|---|---|
| | **Subterranean clover** | |
| Shoot dry weight | $-0.36 + 1.17$ exch.Ca $+ 0.0018$ DOC $- 0.050$ $CaCl_2$(.05M) - Mn $+ 0.050$ DTPA-Mn | 0.87** |
| Shoot Mn concentration | $106.4 + 3.67\ a_{Al}3+ + 29.37$ $CaCl_2$(.01M)- Mn | 0.92** |
| Shoot Mn uptake | $-220.1 + 0.53$ DOC $+ 29.58$ DTPA-Mn | 0.71** |
| Root dry weight | $-0.13 + 0.017$ Ca sat. $+ 0.00053$ DOC $- 0.014$ $CaCl_2$(.05M) - Mn $+ 0.016$ DTPA-Mn | 0.86** |
| Root Mn concentration | $32.11 - 3.82\ a_{Al}3+ + 10.53\ a_{Mn}2+$ | 0.92** |
| Root Mn uptake | $93.40 - 241.3$ Exch. Al $+ 12.89$ DTPA-Mn $+ 2.36\ a_{Mn}2+$ | 0.84** |
| | **Switchgrass** | |
| Shoot dry weight | $4.33 - 1.94$ Exch. Al $+ 0.0034$ DOC $- 0.16$ $CaCl_2$(.05M) - Mn $+ 0.19$ DTPA-Mn | 0.90** |
| Shoot Mn concentration | $97.25 + 2.02\ a_{Al}3+ + 10.33$ $CaCl_2$(.01M)-Mn $+ 0.24\ a_{Mn}2+$ | 0.96** |
| Shoot Mn uptake | $653.2 - 5.76\ a_{Al}3+ + 30.73$ DTPA-Mn $+ 4.83\ a_{Mn}2+$ | 0.89** |
| Root dry weight | $1.25 - 0.55$ Exch. Al $+ 0.0010$ DOC $- 0.070$ $CaCl_2$(.01M) - Mn $+ 0.055$ DTPA-Mn | 0.86** |
| Root Mn concentration | $10.43 + 0.45\ a_{Al}3+ + 2.86$ $H_3PO_4$-Mn $+ 1.97\ a_{Mn}2+$ | 0.97** |
| Root Mn uptake | $-27.41 - 1.53\ a_{Al}3+ - 22.78$ $NH_4OAc$-Mn $+ 7.98$ DTPA-Mn $+ 9.83$ $H_3PO_4$-Mn $+ 2.65\ a_{Mn}2+$ | 0.94** |

[a] Mn uptake = [Dry weight (kg)] [Mn conc. (mg/kg)]

[b] Soil and soil solution properties measured at harvest were used in the regression equations.

**Significant at the 0.01 level.

Exch. Ca = soil exchangeable Ca; DOC = Dissolved organic carbon in soil solution; $CaCl_2$(.05M) - Mn = Mn extracted with 0.05M $CaCl_2$ in 1 hour; DTPA-Mn = Mn extracted with 0.005M DTPA in 2 hours; $a_{Al}3+$ = activity of $Al^{3+}$ in soil solution; $CaCl_2$(.01M)-Mn = Mn extracted with 0.01M $CaCl_2$ in 16 hours; Ca sat. = (exchangeable Ca X 100)/(cation exchange capacity); $a_{Mn}2+$ = activity of $Mn^{2+}$ in soil solution; exch. Al = soil exchangeable Al; $H_3PO_4$-Mn = Mn extracted with 0.033M $H_3PO_4$ in 1 hour; $NH_4OAc$-Mn = Mn extracted with 1M $NH_4OAc$ in 30 minutes.

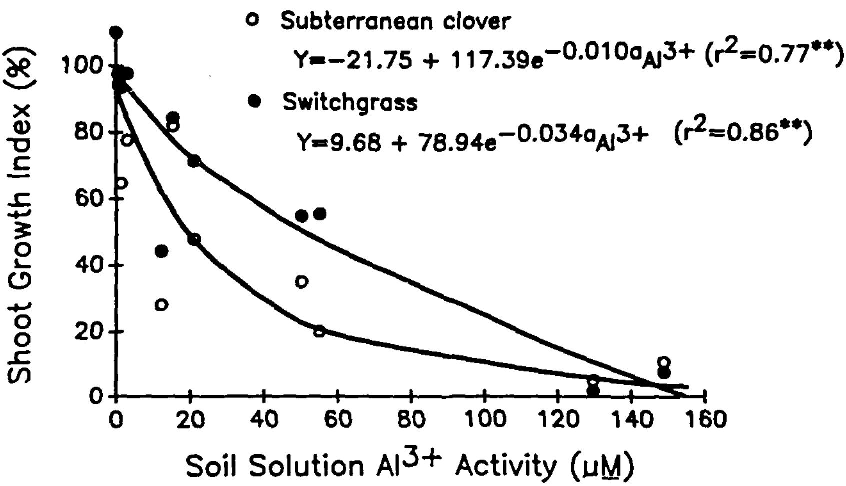


FIGURE 2. Subterranean Clover and Switchgrass Shoot Growth Index (Growth Without Lime x 100/Growth With Lime) as a Function of Soil Solution $Al^{3+}$ Activity in Unlimed Soil Horizons.



Expressions for Mn extracted by $CaCl_2$ (0.01M and 0.05M) and DTPA appear in the regression equations for growth. There is no indication of Mn deficiencies in these soils and an explanation cannot be given for the positive sign associated with the DTPA-Mn term.

Functions of Al as well as Mn appear in the multiple regression expressions for shoot and root Mn concentration and uptake (Table 5). These findings suggest that Al may be controlling plant growth and thereby influencing Mn concentrations and Mn uptake. Expressions for Mn concentrations generally contain a positive term for Al while Mn uptake equations contain a negative Al term. High levels of Al reduce growth and the resulting root injury may lead to passive accumulation of certain elements including Mn (27). This leads to higher tissue levels of Mn, but overall Mn uptake would be lower because of the greatly reduced growth.

Other investigators (8,28) have noted that an exponential relationship usually exists between soil solution Al and plant growth. The shoot growth index (growth without lime x 100/growth with lime) of subterranean clover and switchgrass is plotted as a function of the activity of $Al^{3+}$ in the soil solution of the unlimed horizons (Fig. 2). The shoot growth index of subterranean clover ($r^2$ = 0.77) and switchgrass ($r^2$ = 0.86) are both significantly ($p<0.01$) related to $Al^{3+}$ activity by exponential equations. These results suggest that Al is more important than Mn in controlling plant growth in the soil horizons used in this investigation.



## CONCLUSIONS

Measured and calculated forms of soil solution Mn were more closely correlated with subterranean clover and switchgrass Mn concentrations and Mn uptake than the Mn removed by any of the extractants. The Mn extracted by 0.01$\underline{M}$ $CaCl_2$ was more closely correlated with Mn concentrations and Mn uptake than the Mn obtained with the other extractants. Manganese extractable with 0.01$\underline{M}$ $CaCl_2$ would be easier to obtain than soil solution Mn and would be a suitable substitute for estimating plant available Mn for routine uses. Growth of subterranean clover and switchgrass was significantly depressed in unlimed relative to limed horizons in 9 of 11 and 7 of 11 cases, respectively. Even though high concentrations of Mn were found in the plant materials, both Al and Ca seemed to be more important than Mn in controlling growth in these horizons.

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